Heat Capacity Ratios of Nitrogen (N_2), Carbon Dioxide (CO_2), and Argon (Ar)

Danielle Filer, Isaac Curtis

University of Idaho

Chem307-54

December 9, 2014

Heat capacity is important in explaining certain phenomena, such as why water is a good coolant or why it makes an effective water bath for experiments. There are two different kinds of heat capacities, constant volume, which uses internal energy, and constant pressure, which uses enthalpy. We examined the equipartion theorem, which breaks down the energies associated with each degree of freedom. The three types of energies are rotational, vibrational, and translational. We also looked at the data as a Van der Waal's gas and constant volume heat capacities. We used two different experimental methods to find the heat capacity ratios: adiabatic expansion method and sound velocity method. The results from the sound velocity method matched literature values almost exactly, while the results from the adiabatic expansion method were not as accurate. All of the models we looked at showed that the data for nitrogen was less accurate when vibrational energies were accounted for, carbon dioxide sat somewhere in-between and didn't follow either one, and argon remained the same either way. This is because vibrational contributions at room temperature are very small. It would be best to do more trials and test different gases to further explain the trends of heat capacity ratios. It would be interesting to see how different molecular shapes of atoms affect the heat capacities.

Introduction

Heat Capacity is a measure of the ability of a chemical system to absorb energy for a given increase in temperature in Kelvin. Two common forms of heat capacity are constant volume heat capacity, C_v, and constant pressure heat capacity, C_p. We looked at both constant pressure and constant volume heat capacity for argon, nitrogen, and carbon dioxide. The equation for constant volume heat capacity is $C_v = (\partial U / \partial T)_v$, where U is internal energy. The equation for constant pressure heat capacity is $C_p = (\partial H / \partial T)_p$, where H is enthalpy. We were interested in the heat capacity ratio, $\gamma = C_p / C_v$.[1] We were able to compare the values we received to the ideal gas values of 5/2 R for C_p, 3/2 R for C_v, and 5/2 R for γ.[2] Heat capacity is important, because it describes how substances can absorb heat without a large change in temperature. Water, for example, has a very large heat capacity, allowing it to absorb a lot of heat with only a small increase in temperature. This is the reason why water is a great coolant and also explains why water baths are so effective in experiments. We can describe molecules by degrees of freedom, described in Garland.[2] The number of degrees of freedom for a molecule is given by 3N, where N is the number of atoms in the molecule. There are three different types of degrees of freedom, which are translational, rotational, and vibrational. These classify them by the methods in which they change configuration or position, including bending, stretching, and rotating. For translational there are 3 different degrees of freedom. For rotational there are 2 degrees of freedom for linear molecules and 3 degrees of freedom for non-linear. This is because a linear molecule only requires two axes. In a nonlinear molecule, there is an appreciable magnitude moment of inertia and requires three rotational degrees of freedom to describe its orientation. In a diatomic molecule, such as nitrogen gas, it can only stretch. For vibrational degrees of freedom there are 3N-5 for linear and 3N-6 for non-linear. The equipartition theorem breaks down the energies associated with each degree of freedom. For each degree of freedom, ½RT per mole of kinetic energy is contributed to the total energy; however, vibrational adds an additional ½RT of potential energy. This makes the equation for total internal energy, $U_{Tot} = U_{Trans} + U_{Rot} + U_{Vib}$.[1] Now that we know U, we can use it to calculate the heat capacity ratios. We know that for an ideal gas $C_p - C_v = R$, so we can look at the heat capacity ratio as $C_v + RC_v$. We can also model the results as a Van der Waals gas using the theoretical equation, $\gamma = 1 + \frac{R}{C_v}\left(1 + \frac{2a}{pV^2}\right)$, and the experimental equation, $\gamma = \frac{Mc^2}{RT}(1 - \frac{2a}{pV^2} + \frac{2b}{V})^{-1}$.
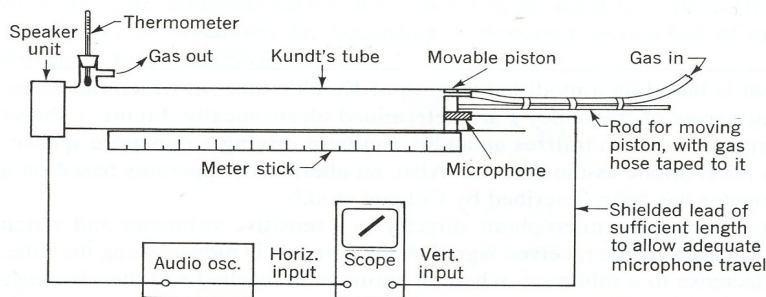
Experimental Procedure

There were two different experimental methods, explained in Garland, that we compared: the adiabatic expansion method and the sound velocity method.[2] For the adiabatic expansion method, we had a carboy connected to the observed gas and a manometer, observed in Figure 1. Gas was flushed through the carboy for 15 minutes to assure only the observed gas was inside the carboy. This was allowed to reach room temperature, which is when P_1 was taken. Then, the stopper was pulled out of the carboy; releasing the gas adiabatically and allowing the pressure inside the carboy come to equilibrium with the room pressure, P_2. The stopper was

Figure 1: Adiabatic Expansion Method[2]
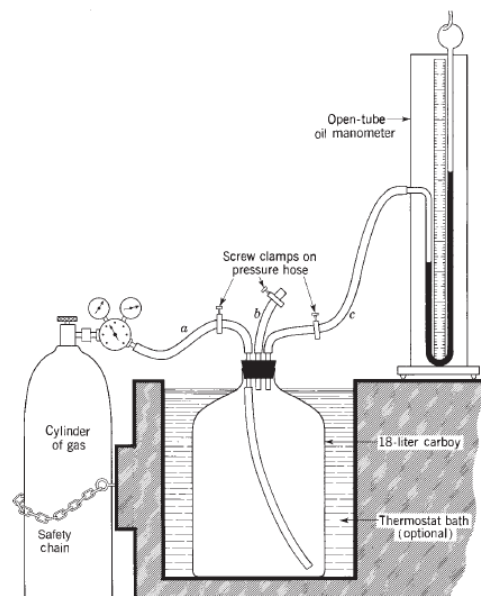
replaced and the system, under constant volume, came back to room temperature for another 15 minutes. After 15 minutes, we recorded the pressure on the manometer, P_3. We were able to calculate the heat capacity ratio from the three pressures recorded with the equation,

$$\gamma = \frac{\ln(P_1)}{\ln(P_2)} \Big/ \frac{\ln(P_1)}{\ln(P_3)}.$$

For the second experimental method, we needed to calculate the speed of sound using Kundt's tube. There was a microphone attached to a movable piston at one end and a speaker unit on the other, both were attached to an oscilloscope, observed in Figure 2. The frequencies we examined were 1kHz for N_2 and CO_2 and 2kHz for Ar. We moved the microphone closer to the speaker until a straight-line pattern was observed on the oscilloscope; this represented a phase shift of 0 or 180 degrees. We continued to move it closer, measuring the distance between each period. From there, we calculated the speed of sound, $c = \lambda * frequency$, where λ is the wavelength. We calculated the wavelength by taking the average of twice the distances for three trials. We plugged the speed of sound into the heat capacity ratio equation, $\gamma = Mc^2/RT$, where c is the speed of sound and M is molar mass.
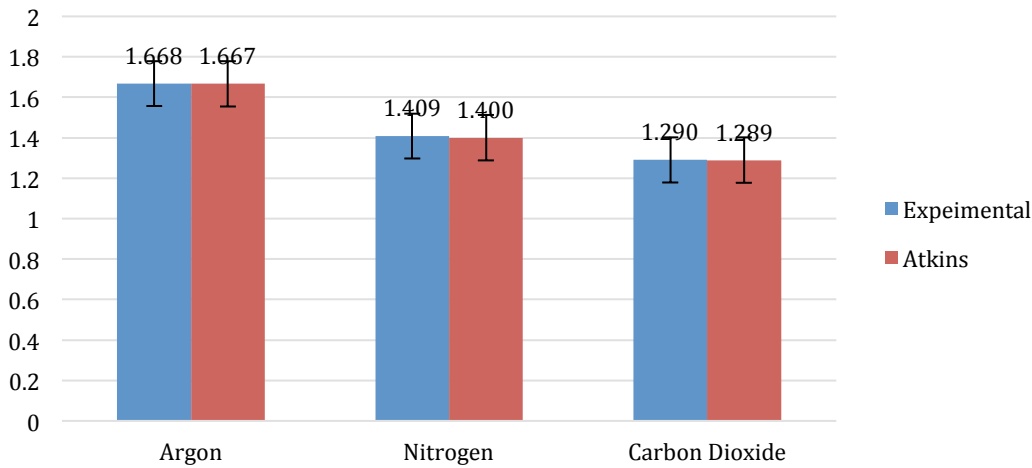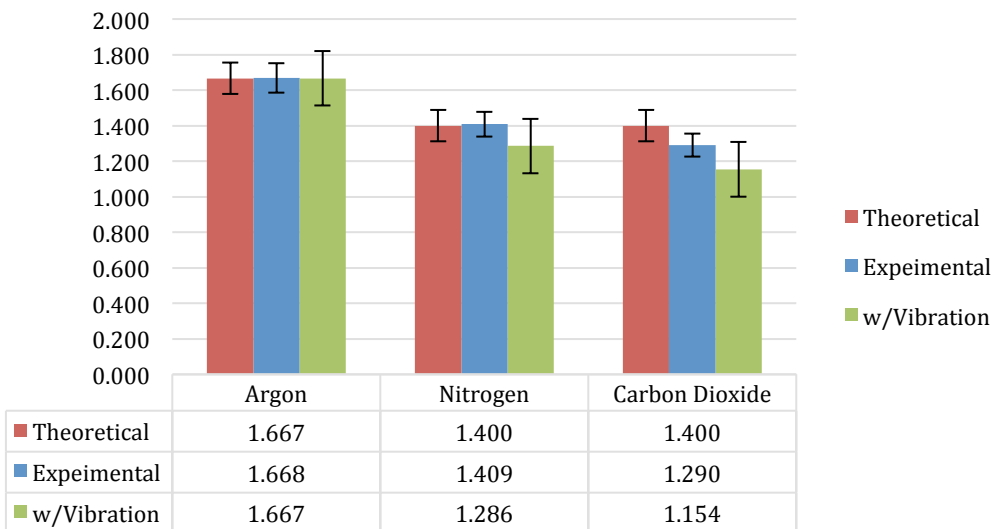

Figure 2. Sound Velocity Method[2]

Results
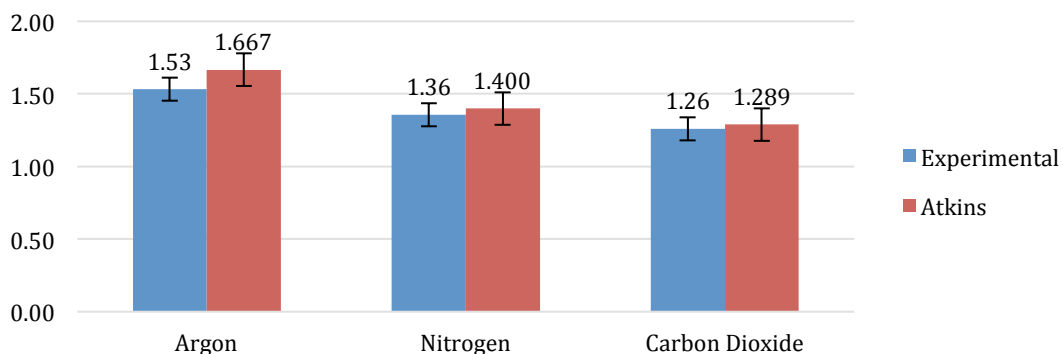
Figure 3: Displays the heat capacity ratios for argon, nitrogen, and carbon dioxide for the adiabatic expansion method compared to the literature values found in Atkins.[3] Values reported with an error of ± 0.01.
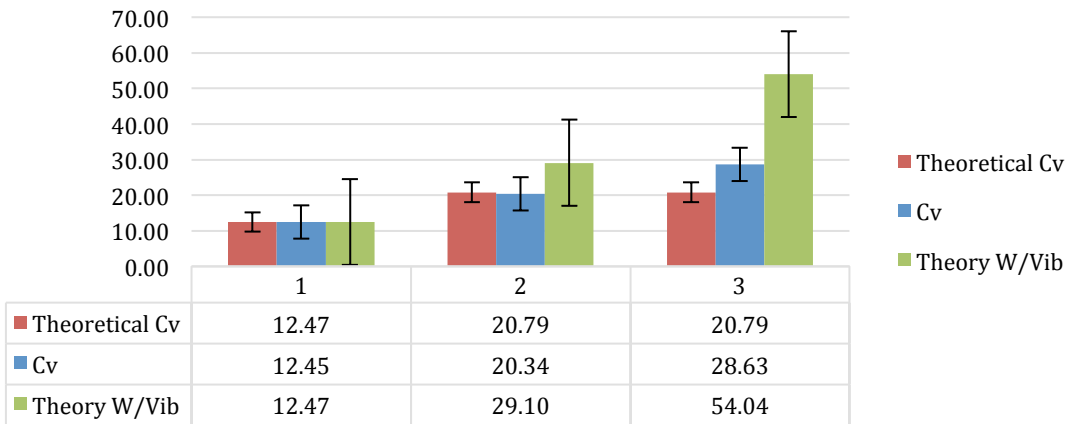
Figure 4. Displays the heat capacities for argon, nitrogen, and carbon dioxide for the sound velocity method compare to literature values found in Atkins.[3] Values reported with an error of ± 0.002.

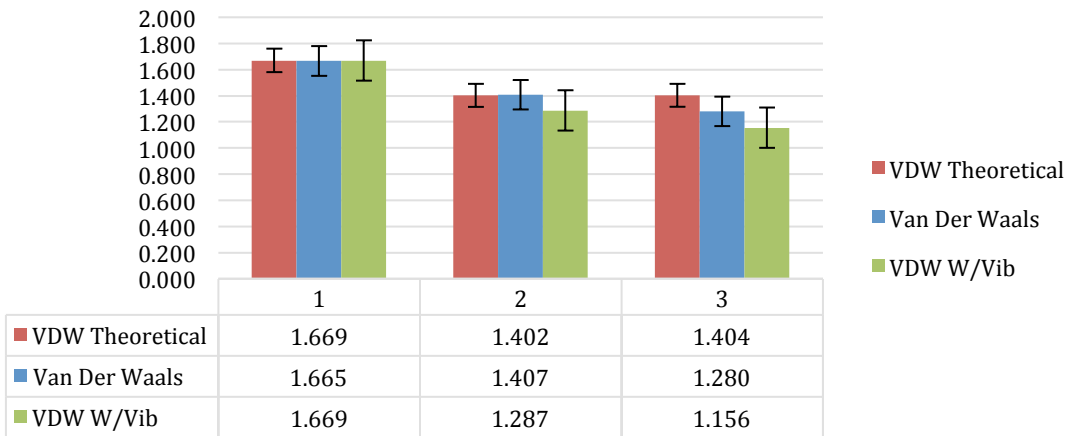|	Argon	Nitrogen	Carbon Dioxide
■ Theoretical	1.667	1.400	1.400
■ Expeimental	1.668	1.409	1.290
■ w/Vibration	1.667	1.286	1.154

Figure 5. Displays the sound velocity method data compared to the equipartition theorem theoretical values with and without vibrational energies. Values are reported with an error of ± 0.002.

Sound Velocity Experimental vs Theoretical Constant Volume Heat Capacities

	1	2	3
■ Theoretical Cv	12.47	20.79	20.79
■ Cv	12.45	20.34	28.63
■ Theory W/Vib	12.47	29.10	54.04

Figure 6. Displays the sound velocity method experimental data compared to theoretical constant volume heat capacities with and without vibrational energy. One is argon, two is nitrogen, and three is carbon dioxide.

Sound Velocity Experimental vs Theoretical Van Der Waals Heat Capacity Ratios

	1	2	3
■ VDW Theoretical	1.669	1.402	1.404
■ Van Der Waals	1.665	1.407	1.280
■ VDW W/Vib	1.669	1.287	1.156

Figure 7. Displays the sound velocity experimental data compared to theoretical values found from Van der Waals equation. One is argon, two is nitrogen, and three is carbon dioxide.

Discussion

The sound velocity method results came out to be a lot more accurate than the adiabatic expansion method. The experimental heat capacity ratios we found for argon, nitrogen, and carbon dioxide for the adiabatic method were 1.53, 1.36, and 1.26 respectively; these values were reported with an error of ± 0.01 and can be found in Figure 3. The experimental heat capacity ratios for argon, nitrogen, and carbon dioxide for the sound velocity method were 1.668,

1.409, and 1.290 respectively; these values were reported with an error of ± 0.002 and can be found in Figure 4. We compared the values for both methods to literature values found in Atkins. The heat capacity ratios in Atkins for argon, nitrogen, and carbon dioxide were 1.667, 1.400, and 1.289 respectively.[3] As shown in Figures 3 and 4, the sound velocity method values are closer to the literature values than the adiabatic expansion. This could be from a variety of different reasons. The biggest reason is because the adiabatic expansion method has a lot of room for error. It is dependent on temperatures being in equilibrium and changing and maintaining the pressure inside the carboy, which makes it more difficult to be accurate. Figure 5 takes a look the heat capacity ratios with vibrational energies using the equipartition theorem. Overall, we found that the theory doesn't match up with the actual results very well. We looked at the sound velocity method to compare, since the results were a lot more accurate. We can see for argon that there is no change in the heat capacity ratio, 1.667, when vibrations are accounted for. This is because argon is a monatomic molecule and can be seen as being nearly ideal, so it follows classical theory really well. Nitrogen and carbon dioxide both have lower heat capacity ratios, 1.286 and 1.154, with vibrational energies included. This is because vibration energy is highly quantized and depends strongly on room temperature. For most gaseous diatomic molecules, such as nitrogen, vibrational contribution is very small, because vibrational modes are only partially active. We would have to see a temperature of 4000K before vibrational contributions in nitrogen are seen.[3] For carbon dioxide, it doesn't follow either theory very well. The equipartition theorem can only be used to calculate the limits of vibrational contribution in polyatomic models. We also looked at theoretical constant volume heat capacities, which were 12.47, 20.79, and 20.79 for argon, nitrogen, and carbon dioxide. Our experimental results for the sound velocity method came out to be very similar, besides for carbon dioxide, as seen in Figure 6. Again, when taking into account the vibrational energies, the heat capacities are far off for nitrogen and carbon dioxide: 29.10 and 54.04. This is for the same reasons as explained previously. Lastly, we looked at theoretical heat capacities using Van der Waal's equation. These results ended up being similar to the results for the equipartition theorem. The theoretical values we found are displayed in Figure 7 as 1.669, 1.402, and 1.404 for argon, nitrogen, and carbon dioxide respectively, with experimental results of 1.665, 1.407, and 1.280. Like we have seen previously, argon and nitrogen follow classical theory very well, while carbon dioxide doesn't. When adding in vibrational energies, the same trends are seen: nitrogen and carbon dioxide heat capacity ratios are lower, 1.287 and 1.156.

Conclusion

In conclusion, we measured the heat capacity ratios using two different experimental methods. The sound velocity method came to good agreement with literature values, while the adiabatic method was not as accurate. This could have been due to a variety of different things, but most likely the nature of the experiment. The adiabatic expansion method leaves a large room for experimental error, making the data less accurate and further away from literature values. It would be best to run the experiment a few more times to get more accurate data. We also found that when adding vibrational energy to the equation the heat capacity was less accurate, except for argon where it was the same. Nitrogen matched all the theories well without vibrational energy, while carbon dioxide didn't match either very well. This trend was observed no matter what way we looked at the data. We looked at the equipartition theorem, the Van der Waal's, and constant volume heat capacities. All three of these theories had similar results. In order to fully see how the heat capacity ratios vary, it would be smart to examine even more gasses and trials.

It would be interesting to look at gasses at different temperatures with different molecular shapes to see how adding and removing vibrational energies from the equation would change the overall heat capacity ratios.

References

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(2) Garland, C. W.; Nibler, J. W.; Shoemaker, D. P. Experiments in Physical Chemistry, 7th Edition. McGraw-Hill Higher Education, 2003; pp 104 – 116 and 29 - 67.

(3) Atkins, P. W. Physical Chemistry: Science of Biology, 6th Edition. W.H. Freeman & Company, 1997; pp 923 - 927.